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IV.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.RESEARCHES ON THE SUBSTITUTED BENZYL COM-
POUNDS.

NINTH PAPER.

THE SYNTHESIS OF ANTHRACENE AND PHENANTHRENE
FROM ORTHOBROMBENZYL BROMIDE.

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Presented May 14, 1879.

Discovery of Anthracene.

THE first notice of anthracene (under the name paranaphthaline) appears in a paper* on compounds of hydrogen and carbon, published by Dumas and Laurent in 1832. They obtained it in the fractional distillation of coal-tar from the portions with the highest boiling-point, but did not succeed in purifying it, as is shown by the melting-point 180° , and the formula $C_{15}H_8$. Laurent,† in 1835, studied its oxidation product "paranaphthalese" (anthrachinone), and in 1837 ‡ proposed the name anthracene for it; but neither of these papers, nor one § also published by Laurent, in 1839, gives a satisfactory account of the hydrocarbon, as the quantity at his disposal was too small for complete purification.

The first accurate characterization of anthracene is due to Fritzsche,|| who, in 1857, obtained from coal-tar a hydrocarbon with the formula $C_{14}H_{10}$, and melting-point 210° , forming a picric acid compound melting at 170° , but he did not identify it with the anthracene of Laurent. This was reserved for Anderson,¶ who in 1861 re-

* Ann. Chim. Phys., l. 187.

† Ibid., lx. 220.

‡ Ibid., lxvi. 149.

§ Ibid., lxxii. 415.

|| St. Petersburg Acad. Ber., 1857. Journ. pr. Ch., lxxiii. 286.

¶ Ann. Chem. Pharm., cxxii. 294.

peated Laurent's experiments on a larger scale, and showed that his anthracene had the formula $C_{14}H_{10}$, melted at 213° , and was the same as Fritzsche's unnamed hydrocarbon.

In 1867, Fritzsche* described the preparation of his reagent (dinitroanthrachinone), and its use in the detection and purification of hydrocarbons; and Berthelot† reviewed all the previous work upon anthracene, determining its boiling-point 360° for the first time.

The next important paper on the subject appeared in 1869, when Fritzsche,‡ on account of its behavior with his reagent, pronounced anthracene a mixture of two very similar hydrocarbons, which he called photene, melting-point 210° – 212° , and phosene, melting-point 193° .

In the following year (1870) general attention was attracted to anthracene by the appearance of Graebe and Liebermann's famous paper§ on anthracene and alizarine, in which they not only proved that alizarine was dioxyanthrachinone by preparing it synthetically from anthracene, but described a large number of derivatives of anthracene, giving for the first time the melting-point of anthrachinone 273° . They showed, too, that Fritzsche's photene was identical with anthracene, but were unable to obtain his phosene, which Barbier|| four years later showed was probably a mixture of anthracene and phenanthrene.

Syntheses of Anthracene.

In describing the syntheses of anthracene, all those made by the same method will be grouped together, and these groups will be taken up in the order of their discovery.

1. Limpricht¶ was the first (in 1866) who made anthracene synthetically, unless, indeed, one of the products obtained by Märcker,** in 1865, from the action of heat on tolallylsulphide must be considered anthracenesulphide, but there seems to be no sufficient ground for this supposition. Limpricht's method consisted in heating benzylchloride with water in a sealed tube to 190° for eight hours; the products were benzylether, an oil $C_{14}H_{14}$, and anthracene.

* Zeit. für Chemie, 1867, p. 289.

† Bull. Chem. Soc., viii. 231.

‡ Zeit. für Chemie, 1869, p. 387.

§ Ann. Chem. Pharm., Supp., vii. 257. A preliminary notice appeared in 1868, Ber. d. ch. G., p. 49.

|| Comptes Rendus, lxxix. 121.

** Ibid., cxxxvi. 94.

¶ Ann. Chem. Pharm., cxxxix. 308.

Van Dorp,* in 1872, obtained the same result, and proved that the oil $C_{14}H_{14}$, which Limpricht had thought was dibenzyl, is benzyltoluol. Finally Zincke,† in 1874, showed that this reaction resembled that of zinc-dust on a mixture of benzylchloride and benzol, and succeeded in isolating a chloride $C_6H_5CH_2C_6H_4CH_2Cl$ and a complex hydrocarbon. He proved, further, that this synthesis was of little value in determining the constitution of anthracene, since neither anthracene nor benzyltoluol was present in the product of the reaction, but they were formed during distillation by the breaking up of the more complex substances just mentioned.

2. In the year after Limpricht's synthesis was published, Berthelot, in developing his general method for the synthesis of complex hydrocarbons by passing simpler ones through a porcelain tube, heated to redness, obtained anthracene ‡ from toluol (confirmed by Graebe § in 1874), xylol, cumol, and mixtures of benzol with ethylene,|| and of benzol with styrol; also traces of it by heating acetylene to redness in a glass tube over mercury. The same method was applied successfully by Van Dorp ¶ to benzyltoluol, that obtained from benzylchloride toluol and zinc-dust, as well as that from benzylchloride and water; by Kramers ** to phenol (yellow heat); by Claus and Suckert †† to azobenzol; and by Barbier ‡‡ to the mixture of toluol with benzol, and to that of diphenyl with ethylene, although the latter yielded only traces of anthracene. Barbier,‡‡ in 1874, substituted for red-hot porcelain tubes vacuum sealed glass tubes heated to dull redness for a few minutes, and obtained in this way anthracene from benzyltoluol, phenylxylol, diphenylmethan, and liquid ditolyl. While Behr and Van Dorp §§ obtained the same result a year earlier by passing liquid benzyltoluol, or liquid tolylphenylketone over gently heated plumbic oxide. The synthesis from orthotolylphenylketone by the aid of heat has been recently repeated by Ador and Rilliet.||||

3. The next synthesis of anthracene was published in 1872 by Kekulé and Franchimont,¶¶ who obtained a small quantity of anthra-

* Ber. d. ch. G., '72, p. 1070. Ann. Chem. Pharm., clxix. 207.

† Ber. d. ch. G., '74, p. 276.

‡ Bull. Chem. Soc., vii. 222.

§ Ber. d. ch. G., '74, p. 48.

|| Bull. Chem. Soc., vii. 279.

¶ Ber. d. ch. G., '72, p. 1070. Ann. Chem. Pharm., clxix. 207.

** Ann. Chem. Pharm., clxxxix. 131.

†† Ber. d. ch. G., '75, p. 37.

‡‡ Comptes Rend., lxxix. 121, 660, 810. Also, Ann. Ch. Phys., ser. 5, vii. 515

§§ Ber. d. ch. G., '73, p. 753.

|||| Ibid., '79, p. 2298.

¶¶ Ibid., '72, p. 909.

chinone from the by-products of the distillation of calcic benzoate. Their results were confirmed by Behr* and Staedel.†

4. Related to this method is that of Barth and Senfhofer,‡ published in 1873, which consists in heating oxybenzoic acid alone, or with sulphuric acid.

5. In 1873, also, anthracene was first obtained by Zincke's reaction; for, although Zincke§ had not succeeded in finding it, Radziszewski and Zaleski|| got it from zinc-dust benzylchloride and benzol, and Paterno and Filetti¶ by the action of zinc-dust on a mixture of benzylchloride and phenol; the latter, however, think that it is not formed directly, but by a secondary reaction from the benzylphenol, and this view is supported by a paper published in the following year by Zincke and Weber,** who obtained it from a mixture of zinc-dust benzylchloride and toluol, but suppose that all the anthracene is formed by the breaking up of complex hydrocarbons during the subsequent distillation, in the same way that it is formed from the product of the action of water on benzylchloride. More interesting, therefore, is the synthesis of Piccard,†† who obtained anthrachinone by the action of zinc-dust on the chloride of phthalic acid and benzol at 220°.

Under this head should come also the recent experiments of Friedel and Crafts,‡‡ who, among their beautiful syntheses with aluminic chloride, made anthrachinone from the same mixture, and finally of Ador and Rilliet,§§ who, in 1879, obtained it from the chloride of orthotoluylic acid benzol and aluminic chloride.

6. Paterno and Filetti,||| in a paper published somewhat later, in 1873, describe the synthesis of anthracene by the distillation of benzylphenol with phosphoric pentoxide.

7. In the same year appeared a paper by Grimm,¶¶ from Baeyer's laboratory, describing the synthesis of chinizarine from phthalic anhydride hydrochinone and sulphuric acid; while in 1874, Baeyer and Caro,*** found that phthalic anhydride yielded, with phenol, benzol-sulphoacid, anisol, anisic acid, or salicylic acid, either oxyanthrachinone or erythroxyanthrachinone, both of which give alizarine by fusion with potassic hydrate; with pyocatechin, guaiacol, or protoca-

* Ber. d. ch. G., '72, p. 971.

† Ibid., '73, p. 178.

‡ Ann. Chem. Pharm., clxx. 100.

§ Ber. d. ch. G., '73, p. 137.

|| Ibid., '73, p. 810.

¶ Gazz. Chim., '73, p. 121.

** Ber. d. ch. G., '74, p. 1153.

†† Ber. d. ch. G., '74, p. 1785.

‡‡ Comptes Rendus, lxxxiv. 1450.

§§ Ber. d. ch. G., '79, p. 2298.

||| Gazz. Chim., '73, p. 251.

¶¶ Ber. d. ch. G., '73, p. 506.

*** Ibid., '74, p. 968.

technic acid, alizarine; with hydrochinone (see Grimm), chinic acid, thiochronic acid, or the α and β sulphoacids of hydrochinone, chinizarine. Still later, in 1875,* they added chlorphenol, boiling-point 218° , to the list of substances which form chinizarine, and converted chinizarine into purpurine by oxidation.

In his last paper † on phtaleines and their derivatives, published in 1880, Baeyer shows their close relation to the anthracene group, ordinary phthalidine being dioxypheylantranol, while a corresponding compound can be obtained from triphenylmethancarbonic acid.

8. The syntheses of anthrachinone from benzoylbenzoic acid also begin in 1873, when Plascuda and Zincke ‡ obtained a little in oxidizing crude benzyltoluol. In the following year Behr and Van Dorp § made it by oxidizing tolylphenylketone, and somewhat later in the same year converted β benzoylbenzoic acid into anthrachinone || by heating it with phosphoric pentoxide, a process which ran smoothly and yielded 26% of the theoretical amount, whereas the para-acid, under the same conditions, gave no anthrachinone whatever. The formation of traces of anthrachinone from the distillation of calcic benzoate alone, and of benzoic acid with phosphoric pentoxide, they ascribe to the previous formation of β benzoylbenzoic acid. Liebermann ¶ next showed that fuming sulphuric acid produced essentially the same effect as phosphoric pentoxide, converting the β benzoylbenzoic acid into anthrachinone sulphoacid, and suggested that this method might be of technical value in the future. Rotering and Zincke ** obtained a similar result by using phosphoric pentachloride, while Thörner and Zincke †† worked out the process further, and showed that chlorine acting on orthotolylphenylketone produced the same effect. Under this head might also be classed the action of hot plumbic oxide on tolylphenylketone already described in Group 2.

9. Closely related to the preceding group is the synthesis depending on the action of zinc-dust on tolylphenylketone, which was studied by Behr and Van Dorp in 1873; ‡‡ also in 1874, §§ when they proved that the para-compound gives no anthracene, and more recently by Ador and Rilliet. |||

Finally, the occurrence of (10) anthracene among the products of

* Ber. d. ch. G., '75, p. 152.

† Ann. Chem. Pharm., ccii. 36.

‡ Ber. d. ch. G., '73, p. 906.

§ Ibid., '74, p. 16.

|| Ibid., p. 578.

¶ Ibid., p. 805

** Ber. d. ch. G., '76, p. 631.

†† Ibid., '77, p. 1477.

‡‡ Ibid., '73, p. 753.

§§ Ibid., '74, p. 16.

||| Ibid., '79, p. 2298.

the action of potassic nitrite on benzylchloride,* and of (11) anthrachinone from the oxidation of isotropic acid † should be mentioned.

Discovery and Syntheses of Phenanthrene.

It is highly probable that Fritzsche,‡ in 1867, encountered phenanthrene in studying the higher fractions of coal-tar with his reagent, as he describes a hydrocarbon melting near 100°; this observation was entirely overlooked, however, and we owe the first definite statements about phenanthrene to Fittig,§ who announced its discovery in August, 1872; but his preliminary notice of it was so imperfect that Glaser, who discovered it at about the same time, sent it to Graebe|| for investigation as a new hydrocarbon. In 1873 three independent tolerably complete accounts of it appeared almost simultaneously in the *Annalen der Chemie*; these were by Fittig and Ostermayer,¶ by Graebe,** and by Hayduck.††

In Graebe's article the synthesis of phenanthrene by passing stilbene or dibenzyl through a red-hot tube is described, whereas Dreher and Otto,‡‡ who tried the same experiment in 1870, before the discovery of phenanthrene, naturally overlooked it.

In the following year Graebe §§ added toluol to the substances, which form phenanthrene under these conditions; and Barbier ||| announced that Fritzsche's phosene (see page 64) was a mixture of anthracene and phenanthrene, since he succeeded in getting the characteristic test, brown plates, with Fritzsche's reagent (dinitroanthrachinone) from such a mixture. Armed with this test, he then proceeded to examine the anthracenes from various syntheses, and found phenanthrene in those made by the action of heat on styrol and benzol, ethylene and benzol, benzyltoluol, phenylxylol, and diphenylmethane; also in the anthracene made from benzylchloride by heating with water, and in that from natural alizarine by reduction with zinc-dust; as in all these cases the phenanthrene could not be detected by any other test except Fritzsche's reagent, there seems good reason for receiving these results with caution, especially as he himself has proved by direct experiment ¶¶ that anthracene cannot be converted into phe-

* Brunner, Ber. d. ch. G., '76, p. 1744. ¶ Ann. Chem. Pharm., clxvi. 361.

† Fittig, Ber. d. ch. G., '79, p. 1739. ** Ibid., clxvii. 131.

‡ Zeitschr. fur Chem., '67, p. 293. †† Ibid., clxvii. 177.

§ Ber. d. ch. G., '72, p. 933. ‡‡ Ibid., cliv. 176.

|| Ibid., p. 968. §§ Ber. d. ch. G., '74, p. 48.

||| Comptes Rendus, lxxix. 121, 660, 810; Ann. Chim. Phys., ser. 5, vii. 515.

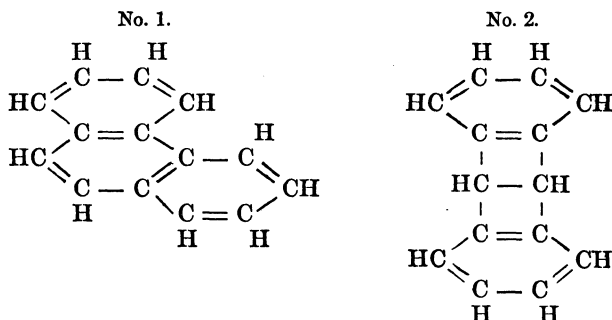
¶¶ Ann. Chim. Phys., ser. 5, vii. 515.

nanthrene by heat. By passing a mixture of ethylene and diphenyl through a red-hot porcelain tube, however, he obtained a large quantity of phenanthrene, and also by heating liquid ditolyl or stilbene to dull redness in a sealed tube. Finally Kramers* found a trace of phenanthrene among the products from passing phenol through a yellow-hot tube.

Constitution of Anthracene and Phenanthrene.

Dumas and Laurent, in their first article on anthracene, considered it a polymerized naphthalene. Anderson, after establishing the formula, called attention to the fact that anthracene and anthrachinone differed from stilbene and benzil only by two atoms of hydrogen in each case. Berthelot, in 1867, on account of its formation from toluol at a red heat, gave it the formula $C_6H_4[C_6H_4C_2H_2]$,† which he showed later in the same year was supported also by Limpricht's synthesis, and his own decompositions of anthracene‡ with hydriodic acid; he considered it an "acetylodiphenylene," but pointed out the fact that, while the calculated boiling-point of this substance should be 310° – 320° , the boiling-point of anthracene is in reality 360° .

In 1870, Graebe and Liebermann proposed two formulas for anthracene, giving the preference to No. 1, on the ground of the syntheses



by Limpricht from benzylchloride, and Berthelot from styrol and benzol; also because this formula is like that of naphthalene, which they show is allied to anthracene in many respects; but these arguments were overturned in 1872 by the discovery of phenanthrene,

* Ann. Chem. Pharm., clxxxix. 132.

† Calculated to modern atomic weights.

‡ Bull. Chem. Soc., ix. 295.

which not only resembled naphthaline more closely than anthracene did, but yielded diphenic acid and other undoubted derivatives of diphenyl, and was therefore entitled to the first formula, leaving the second for anthracene. This arrangement of the formulas was confirmed by Van Dorp's synthesis of anthracene from benzyltoluol, and by some experiments by Graebe,* which showed that phenanthrene-chinone gave diphenyl on distillation with soda-lime, while anthrachinone gave benzol and a very little diphenyl, indicating that there is no direct union of the rings in the latter.

Finally the syntheses from phthalic acid, and the formation of phthalic acid by oxidation, or the action of sulphuric acid † on anthrachinone, established without doubt the ortho position of the connecting atoms of carbon in one of the benzol-rings of anthracene, which was still further confirmed by the syntheses from liquid benzyltoluol and β benzoylbenzoic acid.

At the end of 1873, therefore, the second formula had been universally adopted as that of anthracene, although the position of the two connecting atoms of carbon in one of the benzol rings had not been determined, and the researches of following years, while confirming the points already established, threw no more light on this subject.‡

With phenanthrene the case is different, as the proof of the ortho position of the two additional atoms of carbon has not been neglected. In 1878 Schmitz § argued that this was probably the constitution from the fact that diphenyleneketone and diphenylcarboxylic acid were completely destroyed by oxidation; while somewhat later in the same year the point was proved by Schultz,|| and by Anschütz and Japp,¶ almost simultaneously. Schultz did this by converting Griess's metadiamidodiphenic ** acid (made by the reduction of metanitrobenzoic acid with tin and hydrochloric acid) into diioddiphenic acid, and reducing this to a diphenic acid, which he proved was identical with that from phenanthrene (a proof which he did not make perfectly

* Ber. d. ch. G., '73, p. 63.

† Weith and Bindschedler, Ber. d. ch. G., '74, p. 1106.

‡ Anschütz (Ber. d. ch. G., '78, p. 1213) made diphenyleneketone by heating anthrachinone with calcic oxide, but proves in the same paper that this reaction cannot be used as an argument in regard to the position of the C_2H_2 group in anthracene.

§ Ann. Chem. Pharm., cxviii. 115.

|| Ann. Chem. Pharm., cxvi. 1. Ber. d. ch. G., '78, p. 215.

¶ Ber. d. ch. G., '78, p. 211.

** Ibid., '74, p. 1609.

satisfactory till a later paper,* in 1879). Anschütz and Japp oxidized the sodic salt of the phenanthrenesulphoacid with potassic permanganate, and obtained phthalic acid as the only product, whereas, if phenanthrene were not a diortho compound, isophthalic or terephthalic acid must also have been formed.

In 1879 Merz and Weith † proposed a new formula for phenanthrene, $\text{C}_6\text{H}_4 = \overset{\text{H}}{\text{C}} - \overset{\text{H}}{\text{C}} = \text{C}_6\text{H}_4$, founded on the fact that they obtained invariably perchlorbenzol instead of perchlordiphenyl by the exhaustive action of chlorine upon it; the formation of diphenic acid would then be due to an atomic transformation during the process of oxidation. This hypothesis, however, can hardly be considered as throwing doubt on the constitution of phenanthrene until supported by additional facts, especially since Japp ‡ has shown by the formation and properties of the β phenanthrenecarboxylic acid that the C_2H_2 group behaves as if it were part of a benzol ring.

At present, then, the constitution of phenanthrene must be considered as settled, while it still remains to prove the position of the two connecting atoms of carbon on one of the benzol rings in anthracene.

Action of Sodium on Orthobrombenzylbromide.

In the hope of settling the constitution of anthracene we have studied the action of sodium on orthobrombenzylbromide, since this might lead to the formation of a hydride of anthracene by the union of two molecules, the side-chain of each being joined to the ring of the other, and of phenanthrenedihydride if the two side-chains and the two rings were united. As these two reactions were likely to take place side by side, we expected that our product would consist of a mixture of these two hydrocarbons.

Orthobrombenzylbromide dissolved in anhydrous ether § was warmed with sodium for some days, fresh shavings of sodium, or sodium shot, || being added from time to time, until the bright surfaces were no longer tarnished. The greater part of the sodium was then removed, and,

* Ber. d. ch. G., '79, p. 235.

† Ibid., p. 677.

‡ Ibid., '80, p. 573.

§ When toluol was used in place of ether, the reaction ran so slowly that even after boiling for several days the sodium was but little affected.

|| The sodium shot was made by melting sodium under toluol, and shaking (Wislicenus, Ann. Chem. Pharm., clxxxvi. 212). It seemed not to be so effective as thin shavings of sodium.

after treatment with dilute alcohol to destroy the remainder, the product of the reaction thoroughly washed with water; the yellowish viscous mass thus obtained was oxidized with chromic anhydride, and upon subliming the product, after removing the portions soluble in water and sodic hydrate, yellow needles were obtained which melted at 273° , and gave with zinc-dust and sodic hydrate a red color; they were therefore *anthrachinone*.

0.5745 gr. of the substance gave on combustion 1.7000 grs. CO_2 and 0.2180 gr. H_2O .

	Calculated for $\text{C}_{14}\text{H}_8\text{O}_2$.	Found.
Carbon	80.75	80.67
Hydrogen	3.84	4.21

The anthrachinone was further converted into the bromine compound, which, by fusion with potassic hydrate yielded alizarine.*

A second portion of the orthobrombenzylbromide treated with sodium, and afterward freed from it in the same way, was distilled with steam for a long time; a white substance passed over solidifying in part in the condenser, which was proved to be dibenzyl by its odor, its melting-point 52° , and the following analysis:—

0.2435 gr. of the substance gave on combustion with PbCrO_4 † 0.8240 gr. CO_2 and 0.1700 gr. H_2O .

	Calculated for $\text{C}_{14}\text{H}_{14}$.	Found.
Carbon	92.31	92.27
Hydrogen	7.69	7.75
	<hr/> 100.00	<hr/> 100.02

No anthracenedihydride could be found in the distillate with steam, although it was carefully searched for.

The residue left in the flask, after the distillation with steam, was a yellow viscous mass, which can be most conveniently purified after distillation *per se*, as this destroys the greater part of the viscous substances containing bromine, which render the extraction with a solvent toilsome and unsatisfactory. The distillate, which passed over without a pause from 260° to redness, consisted of a solid mixed with oil, and had a very disagreeable rank smell, different from that of the

* A preliminary notice of the work up to this point was published, Ber. d. ch. G., '79, p. 1965.

† Owing to the ease with which the substance sublimes, great difficulty was encountered in getting a satisfactory combustion.

undistilled substance. The less volatile parts of the distillate were easily converted by washing with alcohol and ether into white plates with a blue fluorescence, which melted at 212° , and were therefore *anthracene*. The residue left by evaporation of the alcoholic washings consisted of dibenzyl, a brown viscous substance containing bromine, and a small amount of a yellow oil: it was tested for phenanthrene by oxidation with chromic anhydride in glacial acetic acid solution, and treatment of the product, after it had been freed from chromic compounds with water, and from acids by weak sodic hydrate, with warm acid sodic sulphite; the solution thus formed was filtered, acidified with hydrochloric (better nitric) acid, and allowed to stand for some time, when it deposited a yellow precipitate, which melted at 198° , and was therefore *phenanthrenequinone*. For further confirmation it was tested, according to Laubenheimer,* as follows: a little of the substance was dissolved in about 5 cc. of glacial acetic acid, a few drops of toluol, and 8–10 drops of sulphuric acid were added, and the mixture allowed to stand over night. It was then poured into water, which, shaken with ether, imparted to it a deep claret-red color, exactly like that obtained from pure phenanthrenequinone under the same conditions.

In a third experiment 20 grammes of orthobrombenzylbromide were treated with sodium for nearly a month in the way already described, but, instead of adding water at once to the product, the organic matter was extracted from the sodium and sodic bromide as far as possible with ether and benzol, in order to avoid the reducing action of the hydrogen set free by water. The residue insoluble in these solvents was finally treated with water, and the small amount of organic matter thus obtained added to that at first extracted. The amount of dibenzyl in this product was notably smaller than in those which had been treated directly with water. In a weighed portion an attempt was made to determine the amount of phenanthrene, by adding picric acid to a strong alcoholic solution, but no crystals of the picric acid compound of phenanthrene separated; the solution was therefore evaporated, and in this way a few red crystals were obtained, which had the form of the compound of anthracene with picric acid, and melted in the crude state near 168° instead of at 170° ; the quantity was too small to admit of purification. The formation of the anthracene compound, which is decomposed by alcohol, apparently from an alcoholic solution, can be explained by the supposition that it was not formed

* Ber. d. ch. G., '75, p. 224.

until the alcohol had evaporated, leaving the anthracene and picric acid dissolved in the oily impurities. In point of fact, it was obtained by imitating the above conditions; that is, evaporating an alcoholic solution of anthracene and picric acid, to which a few drops of toluol had been added. The experiment would seem to show that phenanthrene as such does not exist in the original product.

To meet the objection, which might be urged, that the anthracene obtained in the second experiment was not formed directly by the action of sodium on the orthobrombenzylbromide, but during the distillation of the viscous mass, which resembled the substance obtained by Zincke both from his reaction and the action of water at high temperatures on benzylchloride, another portion was treated with ether and hot alcohol, which removed a yellow oil and left *anthracene* identified by crystallizing in white plates melting at 210° . The yellow oil contained either phenanthrene or its dihydride,* as it gave phenanthrenequinone by oxidation, but we were unable to determine which of these substances was present on account of the small amount at our disposal. We are therefore in doubt as to the way in which the phenanthrene occurs in our product; for, on the one hand, we could not obtain the picric acid compound either from the original product or the yellow oil, while, on the other, a substance crystallizing in plates melting between 170° and 190° , which has appeared more than once in the course of this work as an intermediate product in the purification of the anthracene, yields on oxidation anthrachinone and phenanthrenequinone, and seems therefore to be a mixture of the two free hydrocarbons.

No anthracenedihydride could be found in any of the products, nor have we succeeded in detecting benzyltoluol or ditolyl, although it is highly probable that they were formed in addition to the dibenzyl; but the acids resulting from the oxidation appeared in such small quantities, and so contaminated with a brown impurity formed from the viscous brominated substance, that it was impossible to obtain any definite result from them. The viscous substances, too, containing bromine, which were the principal products of the reaction, have resisted thus far all our efforts to bring them into a form suitable for analysis, but we hope to return to this part of the subject hereafter.

* Phenanthrenedihydride has never been prepared with certainty, although Barbier (*Comptes Rendus*, lxxix. 121) thought it was formed by the reduction of phenanthrene with sodium amalgam.

Finally the following quantitative results were obtained :—

Organic product from 20 grs. orthobrombenzylbromide	10.85 grs.
Calculated product if free from bromine	7.12 “
Bromine not removed by the sodium	3.73 “
Bromine in 20 grs. orthobrombenzylbromide	12.88 “
Bromine removed as bromide of sodium	9.71 “
Bromine not removed by the sodium	3.17 “

The “bromine removed as bromide of sodium” was determined by precipitating 7.727 grs. of the wash-water with argentic nitrate, which gave 1.482 grs. of argentic bromide. As the weight of the wash-water was 119 grs., this corresponds to the result given above. The two determinations of the amount of bromine not removed by the sodium agree as closely as could be expected when the losses resulting from the repeated extraction and washing of the viscous organic products are taken into account.

75.4 per cent of the whole amount of bromine contained in the orthobrombenzylbromide was therefore removed by the sodium.

Determination of the Amount of Anthracene by Luck's Method.*—1.04 grs. of the product, oxidized, first with chromic anhydride dissolved in glacial acetic acid, and afterward with an alkaline solution of potassic permanganate, gave 0.158 gr. of anthrachinone, corresponding to 0.135 gr. of anthracene, that is, 1.409 grs. from the 20 grs. of orthobrombenzylbromide used, or 19.78 per cent of the theoretical yield.

Determination of the Amount of Phenanthrene.—2.44 grs. of the original product, oxidized carefully by adding a strong aqueous solution of chromic anhydride to a hot solution of the substance in glacial acetic acid as long as a drop of the oxidizing agent made the liquid boil,† on extraction of the product with acid sodic sulphite and acidification with nitric acid, yielded 0.05 gr. of phenanthrenechinone, which corresponds to 0.0428 gr. of phenanthrene; that is, from 20 grs. of orthobrombenzylbromide 0.190 gr., or 2.66 per cent of the theory. The amount of phenanthrene actually formed must have been somewhat larger than this, as some of the chinone was undoubtedly destroyed by the chromic anhydride,—in fact, the operation can hardly be called a quantitative one.

* Zeitschr Anal. Chem., '73, p. 347; '74, p. 251.

† Liebermann and Hörmann, Ber. d. ch. G., '79, p. 591.

From the work described above, it appears that 20 grs. of ortho brombenzylbromide yielded, —

Total organic product	10.850 grs.
Anthracene	1.409 “
	<hr/>
	9.441 “
Phenanthrene	0.190 “
	<hr/>
	9.251 “
Dibromdibenzyl, or its isomeres, calculated from 3.17 grs. of unremoved bromine	6.738 “
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Undetermined, containing phenanthrene, dibenzyl, benzyltoluol, and ditolyl	2.513 “

Summary of Results.

Orthobrombenzylbromide when treated with sodium yields anthracene (identified by its melting-point 212° , the formation of anthrachinone melting-point 273° , and of alizarine; 19.78% of the theoretical yield); and phenanthrene (identified by the melting-point of its chinnone 198° , and by Laubenheimer's test; 2.66% of the theoretical yield). Certainly part, and probably all, of the anthracene occurs in the free state; no anthracenedihydride could be found. Our experiments leave us in doubt as to the way in which the phenanthrene occurs. Dibenzyl was also obtained, an oil possibly benzyltoluol or ditolyl, and a viscous substance containing bromine.

By this synthesis of *anthracene* from orthobrombenzylbromide, it is proved that the *two connecting carbon atoms are attached to each ring in the ortho position*, and thus the last doubt about the constitution of anthracene is removed.

The synthesis of phenanthrene, while it confirms the ortho attachment of the two additional atoms of carbon, proves nothing either for or against the formula recently proposed by Merz and Weith.

The publication of the preliminary notice of this work, already mentioned, drew out an article from Von Pechmann,* describing work done at about the same time as ours, in which he applies to anthracene the ingenious method contrived by Graebe for determining the

* Ber. d. ch. G., '79, p. 2124.

constitution of naphtaline as follows: bromorthobenzoylbenzoic acid, prepared by the action of bromphthalic acid on benzol in presence of aluminic chloride, was converted into bromanthrachinone by heating with sulphuric acid, which on fusion with potassic hydrate gave erythoxyanthrachinone, and, as this when oxidized yielded phthalic acid, the conclusion drawn from our experiments that anthracene is a diortho substance is confirmed by his work.